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Electrochemical Dearomative Carboxylation of Electron-deficient Aromatic Compounds

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Dearomative carboxylation of stable aromatic compounds from nucleophilic CO_2 radical anion species is a powerful method for producing synthetically useful carboxylic acids. This radical species could readily be prepared electrochemically or photochemically. Recently, our group reported the electrochemical method for the dearomative dicarboxylation of heteroaromatics utilizing CO_2 , and the photoredox method for the analogous monocarboxylaion of heteroaromatics and electron deficient aromatic compounds by using cesium formate as a C1 source.^{1,2} Encouraged by these findings, we herein describe a new methodology using electrochemical strategy for the reductive carboxylation of electron-deficient naphthalene derivatives with CO_2 that produces unprecedented *trans*-oriented carboxylic acids with respect to the electron-withdrawing group on the naphthalene ring as a major diastereomer.

Under the similar conditions for the electrochemical dearomative carboxylations of heteroaromatics,¹ the reaction of methyl 2-naphthoate furnished a complex mixture of unselectively mono- or dicarboxylated products. To improve the low chemo- and regioselectivity, a catalytic amount of a polyaromatic hydrocarbon, which could work as a mediator in redox process of electrochemical carboxylation,³ was found to be effective in the present reaction. Reaction with 20 mol% of polyaromatic hydrocarbon was found to be effective to furnish carboxylation at C1-position selectively along with a minor regioisomer.



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